The GEO-SEQ Project
Quarterly Status and Cost Report
September 1, 2001 – November 30, 2001

Project Overview:

The purpose of the GEO-SEQ project is to establish a public-private R&D partnership that will:

- Lower the cost of geologic sequestration by: (1) developing innovative optimization methods for sequestration technologies with collateral economic benefits such as enhanced oil recovery (EOR), enhanced gas recovery (EGR), and enhanced coalbed methane production, and (2) understanding and optimizing trade-offs between CO_2 separation and capture costs, compression and transportation costs, and geologic sequestration alternatives.

- Lower the risk of geologic sequestration by: (1) providing the information needed to select sites for safe and effective sequestration, (2) increasing confidence in the effectiveness and safety of sequestration by identifying and demonstrating cost-effective monitoring technologies, and (3) improving performance-assessment methods to predict and verify that long-term sequestration practices are safe and effective and do not introduce any unintended environmental impacts.

- Decrease the time to implementation by: (1) pursuing early opportunities for pilot tests with our private sector partners, and (2) gaining public acceptance.

In May 2000 a project kickoff meeting was held at Lawrence Berkeley National Laboratory (LBNL) to plan the technical work to be carried out starting with FY00 funding allocation. Since then work was performed on four tasks: (A) development of sequestration co-optimization methods for EOR, depleted gas reservoirs, and brine formations; (B) evaluation and demonstration of monitoring technologies for verification, optimization and safety; (C) enhancement and comparison of computer simulation models for predicting, assessing and optimizing geologic sequestration in brine, oil and gas, and coalbed methane formations; and (D) improvement of the methodology and information available for capacity assessment of sequestration sites.

This Quarter's Highlights:

- Three-dimensional simulations of CO_2 injection into a depleted gas reservoir, using a five-spot pattern, were expanded. The results showed that the denser carbon dioxide sweeps the natural gas, extending the period during which relatively pure methane can be produced and minimizing CO_2 upcoming in the production well. These results further demonstrate that carbon sequestration with enhanced gas recovery (CSEGR) is physically and technically feasible (Subtask A-2).
- The evaluation of the impact of CO_2 waste stream contaminants on injectivity and sequestration performance continued. A series of breakthrough curves were obtained showing the evolution of pH at specific locations along given flow paths (Subtask A-3).
- As part of a CO_2 EOR project, electrical and electromagnetic measurements were made in the central Vacuum, New Mexico, Field to begin evaluating the impacts, if any, of surface piping and electrical networks on measurements. It was found that field data quality is generally good, with encouraging indications of repeatability and reciprocity (Subtask B-2)
- Stable carbon and oxygen isotope measurements in gases produced by Lost Hills, California, wells show that the isotope signal is only slightly modified as the gases move through the reservoir (Subtask B-3).

- The first workshop on the code inter-comparison project was held in October. Simulation results by different groups showed reasonable agreement for most problems (Subtask C-2).

Papers Submitted, Published or Presented during this Quarter:

Hovorka, S. D., 2001, "Geoscience looks at Global Warming," 45-minutes demonstration for eight-grade students prepared for Earth Science week (October 7-13, 2001).

Law, D. H.-S., 2001, ""Enhanced Coalbed Methane Recovery (ECBM): Production Modeling," paper presented at the Canadian Coalbed Methane Forum (CMF) Third Annual CBM Conference, Calgary, Alberta, Canada, October 10–13, 2001.

Law, D. H.-S., L.H.G. (Bert) van der Meer and W.D. (Bill) Gunter, 2001, "Numerical Simulation Comparison Study for Enhanced Coalbed Methane Recovery Processes, Part I: Pure Carbon Dioxide Injection," paper submitted for presentation at and publication in the proceedings of the SPE/CERI Gas Technology Symposium (GTS) 2002, Calgary, Alberta, Canada, April 30 – May 2, 2002.

Oldenburg, C.M., and S.M. Benson, 2001, "CO_2 injection for enhanced gas production and carbon sequestration," paper submitted for presentation at the 2002 SPE International Petroleum Conference and Exhibition, Villahermosa Mexico, February 2001. SPE paper 74367 and Lawrence Berkeley National Laboratory Report LBNL-49232.

Pruess, K., C.M. Oldenburg, G.J. Moridis, and S.W. Webb, 2001, "Vertical mixing of CO_2 and CH_4 with gravity effects," abstract of paper to be presented at the 2001 Fall Meeting of the American Geophysical Union, San Francisco, December 10-14, 2001, Lawrence Berkeley National Laboratory Report LBNL-48922.

Webb, S.W., 2001, "Modification of TOUGH2 to include the dusty gas model for gas diffusion," Sandia National Laboratories report Sand 2001-3214, October 2001.

Outreach activities

A public outreach effort was initiated. A 45-minute demonstration "Geoscience looks at Global Warming" for an Austin, Texas, based career fair was prepared. It was presented to 600 eight-grade students during Earth Science week (October 7-13, 2001). It provided a low–cost opportunity for informal evaluation of students' background in this area and field-testing of the demonstration and related materials.

Students were generally aware of and interested in global warming, although almost all confused the greenhouse effect produced by CO_2 increase with the polar and atmospheric depletion of ozone. Eighth graders have been introduced to chemistry, but the idea that CO_2 is the major by-product of combustion was new and interesting to them. Students were interested in and somewhat skeptical about pumping a gas or (gas-liquid) underground and expecting it to stay there.

The creation of a Web resource including information and hands-on experiments was proposed. Several proposals to build on the seed money provided by this project are being written. The project will be an example of how research is used to solve current problems and to bring this information to teachers and students. The outreach materials will be designed for two class periods, one defining the need for sequestration (avoid release of CO_2 while extracting energy from fossil fuel) and one exploring how sequestration works (reservoirs, seals, and underground monitoring). The materials will be linked to students' chemistry and earth science studies.

Task Summaries

Task A: Develop Sequestration Co-Optimization Methods.

Subtask A-1: Cooptimization of carbon sequestration, EOR, and EGR from oil reservoirs.

Accomplishments:

- A paper entitled "Screening Criteria for CO_2 Storage in Oil Reservoirs" was accepted for publication in *Petroleum Science and Technology*; it will appear in 2002. As the title suggests, the paper discusses engineering evaluation techniques for choosing reservoirs suitable for CO_2 storage.

Summary:

The objectives of this subtask are (1) to assess the feasibility of co-optimization of CO_2 sequestration and EOR and (2) to develop techniques for selecting the optimum gas composition for injection. Results will lay the groundwork necessary for rapidly evaluating the performance of candidate sequestration sites as well as monitoring the performance of CO_2 EOR.

The initial focus has been to assess the feasibility of CO_2 sequestration in depleted or inactive oil reservoirs. Existing CO_2– EOR selection criteria have been examined in light of the need to maximize CO_2 storage in a reservoir. New criteria have been developed and new approaches for increasing CO_2 storage during EOR have been identified.

Progress this Quarter : Work began on operational models for simultaneous EOR and CO_2 sequestration. This is accomplished through simulating various injection/production/enhanced-oil-recovery scenarios for a synthetic oil and gas reservoir. To date, a synthetic (3-D) reservoir model and a few variations of the model that capture some aspects of geologic uncertainty were created. The model is based upon an actual field.

Work Next Quarter : Once the reservoir models are established, various reservoir development scenarios will be simulated and the simultaneous production of oil and storage of CO_2. will be evaluated. The aim is to establish general principles. For instance, the following alternatives will be examined and contrasted:

1. Gravity drainage by injection into the top structure of a reservoir
2. Water-alternating-gas (WAG) drive mode
3. CO_2 injection early in production life versus late in reservoir life
4. CO_2 injection following waterflooding
5. Stripping of CO_2 from a mixture of CO_2 and N_2 that simulates an incompletely separated combustion gas

Subtask A-2: Feasibility assessment of carbon sequestration with enhanced gas recovery (CSEGR) in depleted gas reservoirs

Accomplishments:

- Three-dimensional simulations in a quarter five-spot pattern for CO_2 injection into a depleted gas reservoir were performed. A SPE paper on this work will be presented at the international SPE conference in Villahermosa, Mexico, in February 2002.

- Simulations of gas-phase diffusion in a gravity-stable configuration to compare the Dusty Gas Model (DGM) and the Advective Diffusive Model (ADM) were carried out. The results will be presented at the Fall 2001 meeting of the American Geophysical Union on December 14, 2001.

Summary:

The objectives of this subtask are to assess the feasibility of injecting CO_2 into depleted natural gas reservoirs for (1) sequestering carbon and (2) enhancing methane (CH_4) recovery. Investigation will include assessments of (1) CO_2 and CH_4 flow and transport processes, (2) injection strategies that retard mixing, (3) novel approaches to inhibit mixing, and (4) identification of candidate sites for a pilot study.

Initial feasibility was assessed through numerical simulation of CO_2 injection into a model system based on the Rio Vista gas field in California. Positive results of this assessment have led to scoping studies for a CSEGR pilot. Industrial partners are now being sought.

In a parallel effort, the numerical simulation capability supporting this assessment is being improved through enhancement to the TOUGH2-EOS7C code. The first improvement was the implementation of a new real-gas-properties module, Gas Eos, which modifies gas-mixture densities and enthalpies using the Peng-Robinson equation of state.

Progress this Quarter : Previous modeling efforts to consider a three-dimensional case, where CO_2 is injected at a lower level in a depleted gas reservoir while CH_4 is produced from a higher level in a quarter five-spot pattern. were extended. Properties of the system were chosen based on the Rio Vista, California, system. The results showed that the higher density of CO_2 causes the gas to sweep from the bottom upward as well as from injector to producer. This effect increases the period over which relatively pure CH_4 can be produced and minimizes CO_2 upcoming to the production well. Plotted in Figure 1 is the mass fraction of CO_2 after eight years of injection and enhanced gas production. As shown, the CO_2 largely occupies the lower portion of the reservoir, as it has effectively displaced CH_4 toward the top of the reservoir. These results are described in the 2001 paper by Oldenburg and Benson.

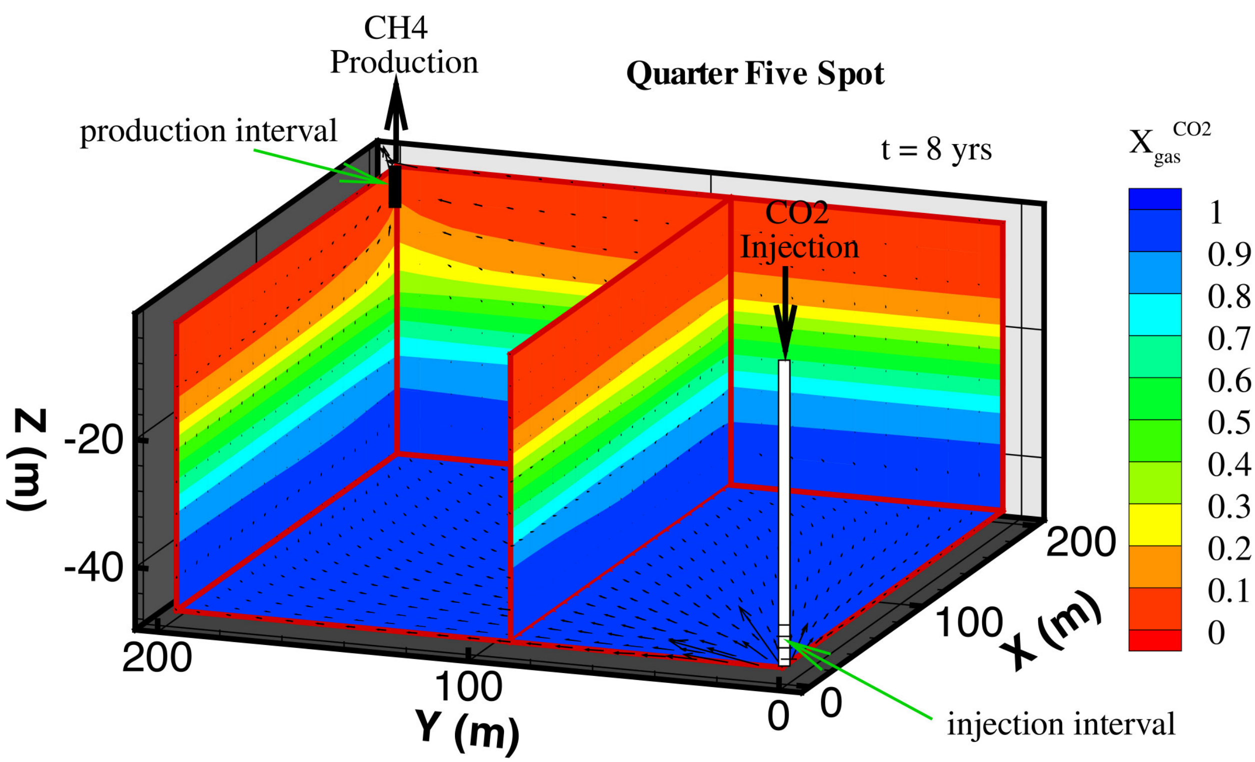

Figure 1. CO_2 mass fraction in the gas after eight years of injection and enhanced gas production.

Comparisons of one-dimensional gravity-stable CO_2-CH_4 interdiffusion using the Advective Diffusive Model (ADM) and the Dusty Gas Model (DGM) were carried out. For the ADM in low-permeability formations, spurious pressure differences arising from mass-conserved diffusion of species with different molecular weights cannot be dissipated by advection. With sufficient permeability, such pressure increases give rise to Darcy flow that dissipates the pressure gradients. Analogous pressure differences do not arise in the DGM. In summary, it was found that the ADM and DGM agree well for all but the lowest permeability cases. Agreement is also good for high-pressure systems such as gas reservoirs with reasonable expected permeabilities. Therefore, it was conclude that the ADM is accurate for modeling gas diffusion processes in this project. At lower pressures, e.g., in the vadose zone, and in low-permeability formations, the DGM is preferred over the ADM because it better handles interdiffusion of species with contrasting molecular weights such as CO_2 and CH_4. Shown in Figure 2 are results that show the differences between the ADM and DGM for CO_2-CH_4 diffusion at 1 bar and 20ºC in a low-permeability formation.

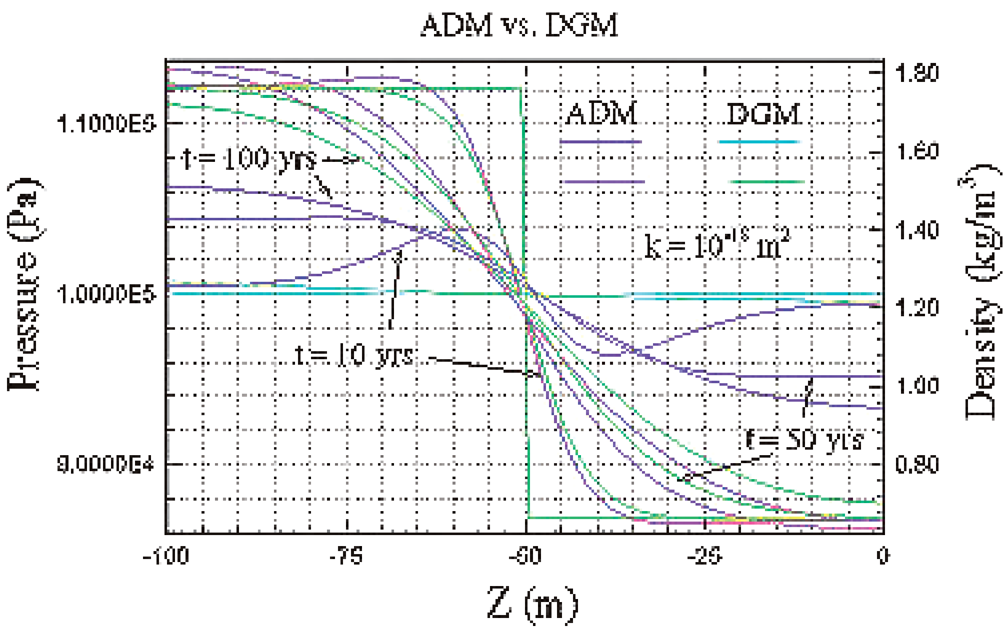

Figure 2. Profiles of pressure and gas density at t = 0, 10, 50, and 100 years during gravity-stable diffusive mixing in the system H_2O-CO_2-CH_4 for the ADM and DGM for a low-permeability formation.

All reservoir and gas property modeling performed to date suggests that CSEGR is physically and technically feasible. The emphasis will turn now to analyses of costs and capacity that could persuade gas producers to give CSEGR a fair evaluation in the field, as a pilot test.

Work Next Quarter :

- Initiate contact with analysts who can assist the team with economic analysis of CSEGR.

- Begin capacity assessments that include consideration of CO_2 solubility in connate water as well as CO_2-CH_4 real gas mixture properties.

- Continue the search for a potential CSEGR pilot site (e.g., through discussions at the SPE meeting in Villahermosa, Mexico).

- Begin development of the users manual for TOUGH2/EOS7C.

<u>Subtask A-3</u>: Evaluation of the impact of CO_2 aqueous fluid and reservoir rock interactions on the geologic sequestration of CO_2, with special emphasis on economic implications.

Accomplishments:

- Reaction progress (closed system) chemical thermodynamic and kinetic simulations were completed that evaluate the impact of waste stream CO_2, as well as contaminants (i.e., SO_2, NO_2 and H_2S), on injectivity and sequestration performance. – Subtask A-3

- Reactive transport (open system) chemical kinetic simulations were begun using the reactive transport simulator CRUNCH (Steefel, 2001). Chemical/mineralogical conditions, including waste stream contaminants, were designed to be analogous to the previously run reaction progress (closed system) simulations, but with the additional consideration of flow added.

Summary:

Lowering the costs of the front-end processes can dramatically lower the overall costs of sequestration. One approach is to sequester less-pure CO_2 waste streams that are less expensive or require less energy to separate from flue gas. The objective of this subtask is to evaluate the impacts of this impure CO_2 waste stream on geologic sequestration.

<u>Progress This Quarter :</u> The evaluation of the impact of waste stream CO_2, as well as contaminants (e.g., SO_2, NO_2 and H_2S), on injectivity and sequestration performance continued. A series of simulations that are equivalent to those that occur along a 1-D flow path using full-dissolution kinetics (including acid catalysis) for all the mineral phases present in the reservoir rock was constructed. The simulation can be visualized as following chemical reactions that take place through space and time along a single streamline. A rock composition and modal abundance appropriate for a feldspathic-sandstone reservoir containing clay and carbonate with an iron-bearing carbonate component were assumed. Earlier work focused on closed-system simulations, while these new simulations add the effect of transport.

As an example of the results obtained, a simulation of the reaction of a NaCl-type brine equilibrated with a supercritical fluid phase consisting of 80 bar CO_2 in the presence of the feldspathic sandstone reservoir rock at 60°C will be described. This simulation with a pure CO_2 phase only will serve as a baseline for subsequent runs designed to investigate the additional impact of other waste stream components (e.g., SO_2, NO_2 and H_2S). The initial composition of the brine is that produced by equilibrating a seawater ionic strength equivalent NaCl solution with the reservoir rock. Then, chemical reactions through space and time along a 50-m length of reservoir rock for a 10-year period is followed as the CO_2-rich brine continuously flows through the rock, displacing the original pore fluid. A linear flow rate of 4 m/y is used, which happens to be the natural (pre-injection) basinal flow rate for the Utsira Formation (Zweigel et al., 2001). This formation is the sandstone reservoir unit being used for CO_2 sequestration in the Sleipner field. In this first simulation it was assumed that in the short-term redox equilibria would be maintained, so the initial fO_2 was set to a value (10^{-60} bar) appropriate for a deep basin whose redox state is determined by hematite-siderite equilibria. The results during 10 years of reaction are presented in Figure 3.

Figure 3 shows a series of breakthrough curves illustrating the evolution of pH through time at specific locations along the length of the flow path. Notice that in this simulation the reservoir rock carbonate minerals (calcite and siderite) at each point along the flow path react quickly with the dissolved CO_2, buffering the pH as they dissolve. The two breaks in slope evident in cell 1 correspond to the time intervals over which first calcite and then siderite dissolve as they buffer the pH. The calcite in cell 1 is completely consumed between years 3 and 4, while sufficient siderite remains to continue buffering pH even after 10 years. Locations further downstream continue to buffer pH to a level (~ pH 4.8) appropriate for equilibrium between the incoming CO_2-rich fluid and the calcite still present at that location. The existing carbonate minerals are not sequestering the waste stream CO_2 in this case, indeed, they are adding CO_2 to the system. Although not shown in the figure, the mineral dawsonite begins to form in cell 1 almost immediately, as soon as the pH drops to a point where the feldspar starts to dissolve appreciably (< pH 6). It forms by combining the sodium from the brine with the aluminum being released by the dissolving feldspar. As the pH front propagates along the flow path, dawsonite begins forming all along the path. Even in the first cell, after approx. three years and all the calcite is consumed and the pH becomes buffered at a lower pH (~ pH 4.3), dawsonite remains a stable secondary mineral. This mineral is sequestering CO_2. As for the reservoir silicate minerals, K-feldspar dissolves continuously throughout the core and over the 10-year time period, as soon as the pH drops, while both quartz and a new silica polymorph, chalcedony, grow along the flow path, serving as sinks for the silicon released by the dissolving feldspar.

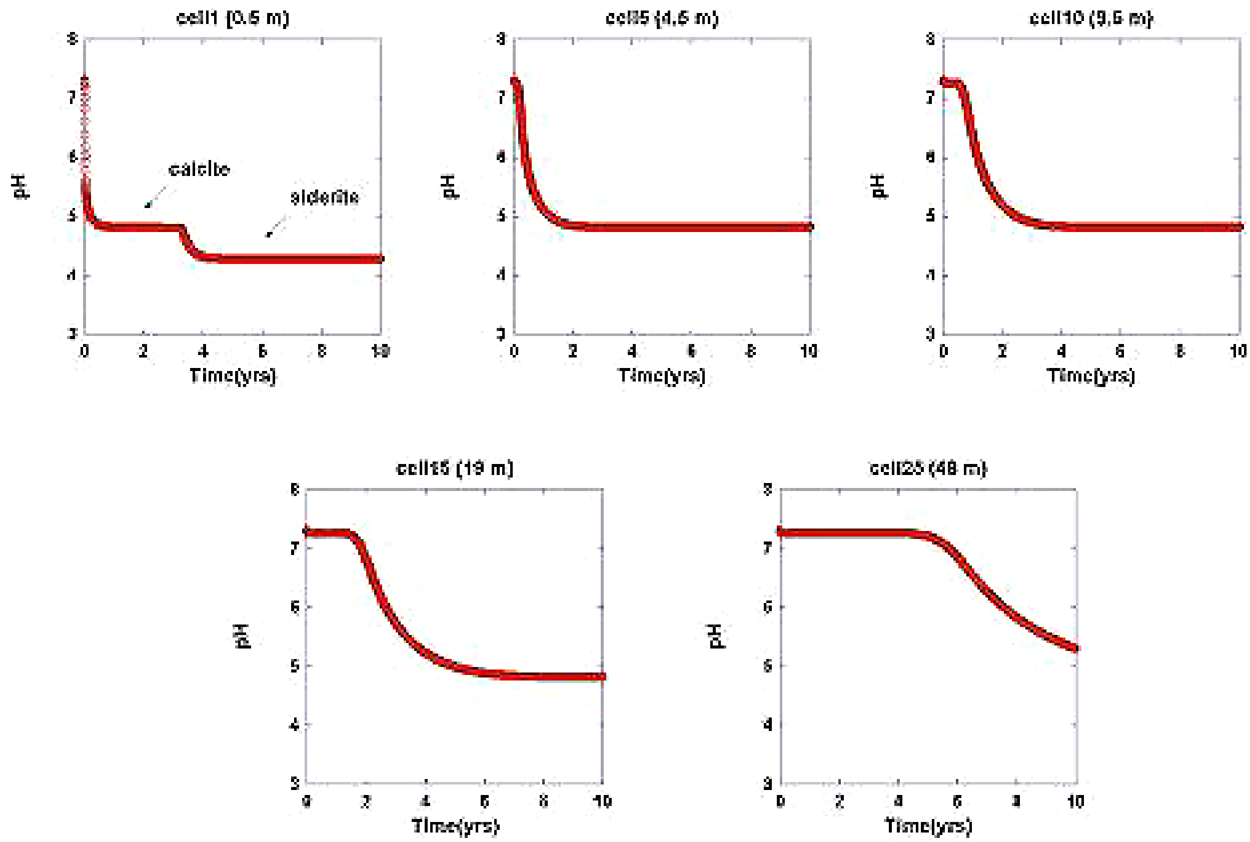

Figure 3. CO_2-pH breakthrough Curves

An overview of accomplishments and progress made during FY01 was presented to NETL program managers and technical staff.

Work Next Quarter : The investigation of the impact of other contaminants (SO_2, H_2S, NO_2, etc.) in the CO_2 waste stream will continue. The process of accounting for the impact of fluid flow on sequestration by conducting open system (reactive transport) calculations analogous to the closed system calculations made previously, is planned.

Task B: Evaluate and Demonstrate Monitoring Technologies

<u>Subtask B-1</u>: Sensitivity modeling and optimization of geophysical monitoring technologies

Accomplishments:

- A strategy for jointly processing and interpreting time lapse crosswell EM and seismic measurements was developed. The process maximizes the spatial correlation between velocity and conductivity images.

Summary:

The objectives of this task are to: (1) demonstrate methodologies for and carry out an assessment of the effectiveness of candidate geophysical monitoring techniques, (2) provide and demonstrate a methodology for designing an optimum monitoring system, and (3) provide and demonstrate methodologies for interpreting geophysical and reservoir data, to obtain high-resolution reservoir images. The Chevron CO_2 pilot at Lost Hills, California, is being used as an initial test case for developing these methodologies (see Subtask B-2 for background information).

Progress this Quarter: Work continued on analysis of the crosswell seismic and electromagnetic (EM) time lapse measurements made to monitor the CO_2 movement in the reservoir. To better constrain the inversion of the data, a processing strategy was developed which would maximize the spatial correlation between velocity and conductivity images. In this approach the conductivity image was used to produce the starting model for Vp inversion and the final Vp model was used as a starting model for Vs inversion. A conjugate gradient algorithm was used to generate a final image which was constrained by the initial model and perturbed only as much as needed to fit the observed data.

The starting model for EM inversion of pre-injection EM crosswell measurements was built by laterally interpolating conductivity logs in the observation wells. The resulting image was used as the starting model for inversion of the post-injection crosswell measurements. The difference of the two inversions gives the time-lapse image of conductivity change shown in panel C of Figure 4.

The starting models for pre- and post-injection EM inversion were converted to Vp models using a rock physics transform derived from logs. These Vp models were used as the starting models for inversion of pre- and post-injection crosswell Vp measurements. The difference of these images gives the time lapse image of Vp change shown in panel 6 of Figure 4.

Finally, the pre- and post-injection Vp images were converted to Vs using a Vp/Vs ratio derived from the rock physics model. Following the same process as described above, the time lapse image of Vs change was obtained as shown in panel a of Figure 4. Note that the Vs data was acquired with an orbital vibrator source with a center frequency of 500 Hz whereas the Vp data was acquired using a piezoelectric source with a center frequency of 2000 Hz. The Vs image is also smoother because Vs is relatively insensitive to changes in water saturation, which has high spatial variability.

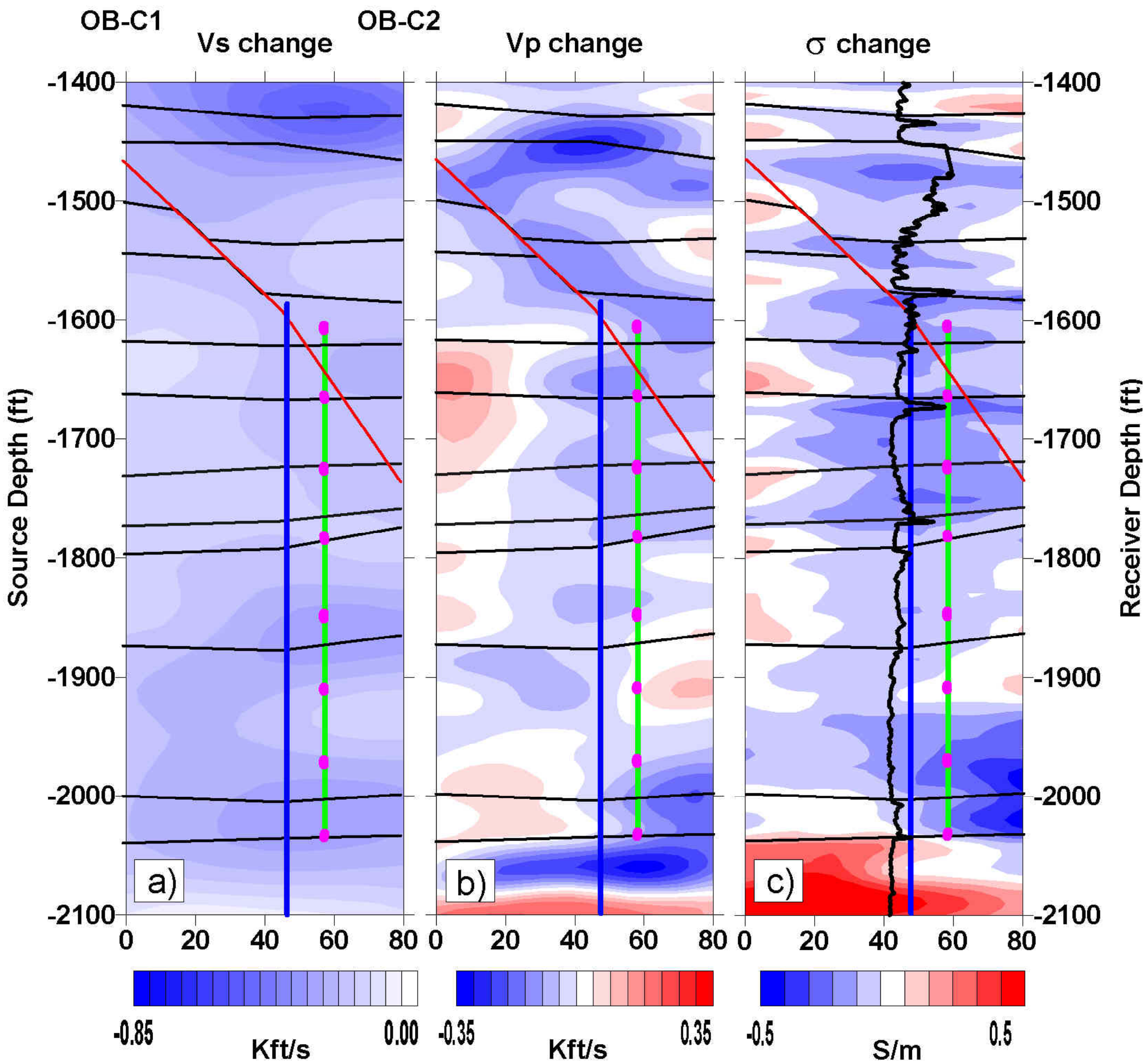

Figure 4. Time-lapse changes in a) shear velocity, b) compressional velocity and c) electrical conductivity. The EM images were used to construct starting models for the Vp inversions and the resulting Vp images were used to construct starting models for the Vs inversions. Major unit boundaries are shown as black horizontal lines, estimated location of previous water injection fracture is shown as vertical blue line, estimated location of the CO_2 injection fracture is shown as a vertical green line, perferation intervals for CO_2 injection are shown as magenta dots, mapped location of a fault zone is shown as the red diagonal line. The permeability log in the out-of-plane CO_2 injection well (11-8WR) is shown in black on panel c).

Work next Quarter: Work will continue on analysis and joint inversion of the crosswell seismic and EM measurements.

Subtask B-2: Field data acquisition for CO_2 monitoring using geophysical methods

Accomplishments:

- Both coarse point electrode and casing ERT surveys were conducted in conjunction with a commercial cross-well EM survey in an oil field undergoing CO_2 flood.
- Numerical simulations were performed to assess signal strength for time-lapse CO_2 monitoring at field site.
- Initial results indicate good data quality for time-lapse work

Summary:

The goal of this subtask is to demonstrate (through field testing) the applicability of single-well, crosswell, surface-to-borehole seismic, crosswell electromagnetic (EM), and electrical-resistance tomography (ERT) methods for subsurface imaging of CO_2.

Progress this Quarter : The primary activity this quarter was to conduct a field program in which baseline electrical and electromagnetic measurements were made in a field in which CO_2 is being injected for enhanced recovery. The field surveys were originally scheduled for September; but due to delays caused by world events the field surveys were conducted in October at ChevronTexaco's central Vacuum Field in New Mexico. ChevronTexaco made both open and cased holes available in the target area, permitting a variety of measurements to be made in the same part of the field. Both a coarse point electrode ERT survey as well as a casing survey were obtained; these ERT surveys were conducted in conjunction with baseline crosshole EM surveys obtained by EMI (a commercial EM survey company).

In general, field data quality is good, with good indications for repeatability and reciprocity. Measurements made using vertical casings in the field, both while connected to surface piping and electrical networks and while disconnected from surface piping, allowing assessment of the actual resistance of the various elements of the subsurface/surface piping network. The variety of hardware at this particular field offers an opportunity to assess the relative influence of both downhole and surface pumping systems as well as different piping configurations. Subsequent time-lapse surveys are planned after CO_2 injection begins in a few months. Questions of data quality, interference and logistics in order to design and conduct safe and effective field surveys that are as transparent as possible to the field operator are being addressed.

Conducting Electrical Resistance Tomography (ERT) surveys using steel casings as long electrodes entails energizing the casings themselves during measurement. While there are plans to electrically isolate the downhole casing from the surface piping and electrical networks using an insulated sub, this is not as simple as it sounds. The great variety of possible hardware configurations at wellheads, particularly pumping systems, present a number of issues. Downhole submersible pumps have electrical lines running from the pump location in the well to surface connections. Rod and sucker pumps have long stands of pump tubing running inside the casing from the pump interval to the surface connections. They in turn commonly have electrical motors connected to surface systems as well. All operational wells have some type of piping leading to distribution networks; these are commonly filled with fluids, although the fluid movement may be periodic or nearly constant. These various configurations present multiple paths for current to flow, which may have adverse impacts ranging from interfering with measurements to safety concerns.

Initial measurements at Vacuum were designed to investigate these issues. The nine-spot of wells used in the survey included three linear sets of wells; two represented lines of producers, the central one is intended for CO_2 injection. Of the six production wells, one was connected to a rod and sucker pump, one had a Rotoflex pump and one submersible pump installed. The three injection wells were not in use during the survey, but two were connected to surface distribution systems. The other four wells were temporarily disconnected from surface distribution systems and had blowout preventers installed at the surface.

The unexpected opportunity to access partially uncased wells in the field made it possible to obtain a cross-well point electrode survey. Two-point electrode strings specially designed and fielded for the purpose were used. These instrumentation strings connected to conventional wireline logging cable, permitting standard logging equipment to be used for the field program. In the target area, the two wells that are open (lacking casing) in the target interval required modification so they could be accessed for a casing survey. To address this issue, specially designed and constructed instrumentation was lowered into each of these wells, simulating the presence of casing to the bottom of each well.

Initial processing of the field data highlighted important issues that need to be considered when working with data collected at such large scale.

The Vacuum field is in active production. In order to work out the logistics for the field program, researchers met with ChevronTexaco staff to identify issues and develop work plans to address them. The original field surveys, originally scheduled for August, were rescheduled for September due to well issues.

Numerical simulations were conducted to assess the expected signal strength during CO_2 injection. Initial results indicate sufficient data above the field-measured thresholds to detect movement of CO_2 over time (Figures 5 and 6).

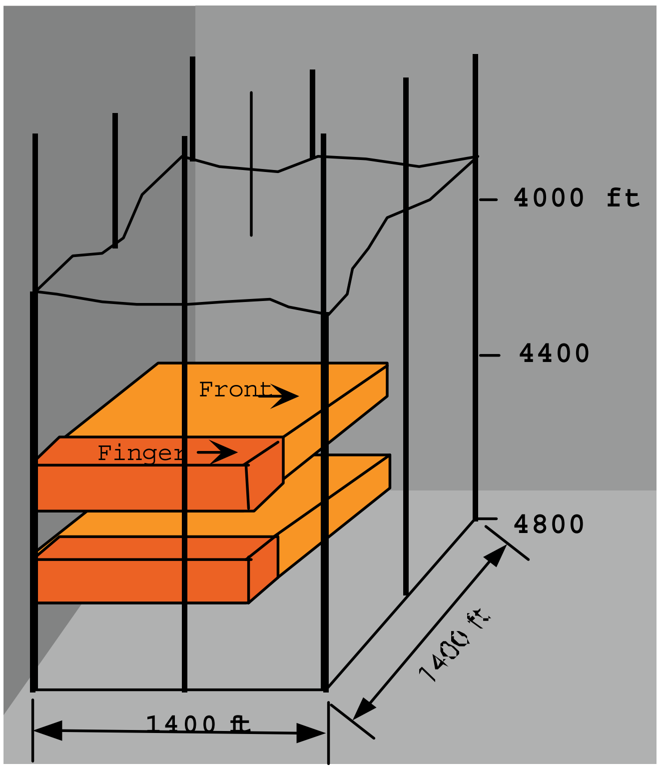

Figure 5. Model used in numerical experiments showing both slab-like fronts and narrow fingers of CO_2 progressing across the reservoir.

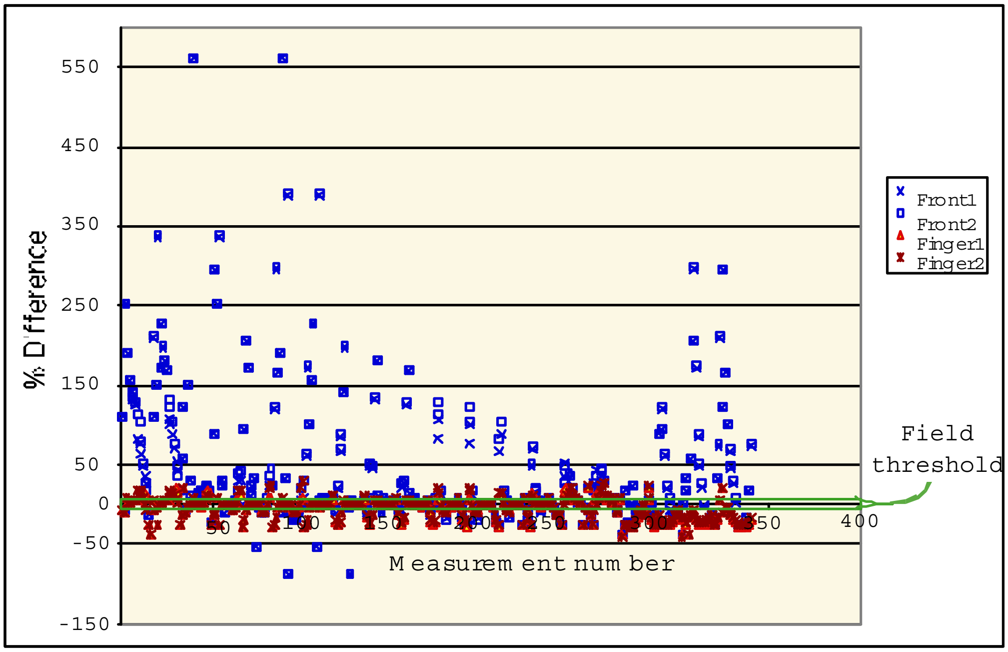

Figure 6. Values of % difference in individual measurements for models simulating narrow fingers or a slab-like fronts moving across the model volume. There are abundant values exceeding the field threshold, which would contribute toward an image indicating the movement of CO_2 over time.

Initial processing of the information highlighted important issues that need to be considered when working with data collected under field conditions. While working on the field surveys, laboratory experiments using physical models in a large water tank were also conducted. These experiments utilize models with both point electrode arrays and long electrodes. In one set of measurements, it was discovered that the resulting image for a casing survey can depend on the measurement schedule. The measurement schedule used in the field at Vacuum was not symmetric, which is most likely effecting the fidelity of the reconstructed image. Since then, symmetric measurement schedules for future field surveys have been developed. Additional testing to verify this result is being done.

Work Next Quarter : The processing and interpretation of baseline survey data will be completed. The results will be discussed with the field operator to improve field design for time-lapse surveys to be conducted after CO_2 injection begins.

The assessment of ERT performance under varying conditions through sensitivity studies will continue.

Subtask B-3: Application of natural and introduced tracers for optimizing value-added sequestration technologies

Accomplishments:

- Stable isotope measurements of carbon and oxygen in gases sampled from wells in the Lost Hills area indicate that the injected CO_2 carbon isotope signal was only slightly modified during migration through the system, probably from mixing with “reservoir” gas.
- CO_2 adsorption-desorption measurements have been made on a standard montmorillonite and compared to the N_2 adsorption-desorption results obtained previously.
- Final design of the dynamic flow system was completed and construction has begun.

Summary:

The overall goal of this effort is to provide methods that utilize the power of natural and introduced tracers to decipher the fate and transport of CO_2 injected into the subsurface. The resulting data will be used to calibrate and validate predictive models used for (1) estimating CO_2 residence time, reservoir storage capacity, and storage mechanisms; (2) testing injection scenarios for process optimization; and (3) assessing the potential leakage of CO_2 from the reservoir.

Progress this Quarter : Gas chromatograph-combustion-isotope ratio mass spectrometry (GC-C-IRMS) was used to characterize the isotopic and gas chemistry of gases from the Chevron Lost Hills, CA system (Figure 7). Carbon and oxygen isotopes were measured in the injection CO_2, CO_2 from pre-injection "reservoir" gases, and the return CO_2 sampled in wells 11-8D, 12-8D, and 12-7. Carbon isotopes have also been measured in C_1-C_6 hydrocarbon gases. The initial injection CO_2 had a $\delta^{13}C$ (PDB) value of –30.1 ‰ and a $\delta^{18}O$ (VSMOW) value of –1.12 ‰. Gases sampled prior to injection were dominated by CH_4 with lesser amounts of CO_2 and subordinate amounts of C_2-C_6. The $\delta^{13}C$ (PDB) values for CH_4 in pre-injection and return gases were very similar, ranging from –36 to –42 ‰. The $\delta^{13}C$ (PDB) values for pre-injection CO_2 ranged from 15.6 to 18.5 ‰ whereas the return CO_2 exhibited a narrow range of values, -27.5 to –29.9 ‰. The return gases were very rich in CO_2 and clearly have values very close to the injection CO_2. This slight modification of the injection CO_2 suggests that it did not come in contact with appreciable amounts of reservoir gas nor did it undergo extensive isotopic shift due to exchange with heavier hydrocarbons in the diatomite. Slight mixing (~5 %) of "reservoir" CO_2 with the return CO_2 might explain the slight enrichment in ^{13}C.

The $\delta^{18}O$ compositions of the pre-injection CO_2 ranged from about 16 to 24 ‰, whereas the return CO_2 gases were somewhat more enriched, ranging from approximately 29 to 34 ‰. This constitutes nearly a 35 ‰ increase in $\delta^{18}O$ from the injection value of –1.1 ‰. Based on the carbon isotope results, it appears that less than 5 % of the reservoir gas may have contributed to the injection CO_2. This small contribution can lead to only a slight enrichment of the ^{18}O in CO_2 – roughly one per mill or so. It is likely that the enrichment in ^{18}O is due to kinetically fast exchange of CO_2 with water encountered during migration. The oxygen isotope fractionation between CO_2 and water is 41.2 ‰ at 20°C, so applying this number to the oxygen values measured for the return CO_2 yields $\delta^{18}O$ values for water of between –7 and –12 ‰. These values are generally consistent with numbers reported for ground waters in this part of CA.

CO_2 adsorption-desorption isotherms were measured at 20°C for montmorillonite using the Quantachrome Autosorb I surface area analyzer. A comparison, with previous measurements on N_2 adsorption-desorption, indicates that CO_2 adsorbs far less than N_2 as expected because of its great molecular diameter. At a total pressure of one atmosphere, N_2 covers the montmorillonite surface at a concentration of roughly 0.26 mmoles/m^2 whereas CO_2 concentration reaches only 0.0076 mmoles/m^2, a difference of nearly 1.5 orders of magnitude. Both gases exhibit concave upwards adsorption trends for plots of moles/m^2 (y-axis) plotted versus log pressure (x-axis), with N_2 displaying a much flatter initial trend indicative of adsorption on prismatic crystal faces. Overall, however, adsorption for both gases is dominated by the basal plane surfaces of the clay.

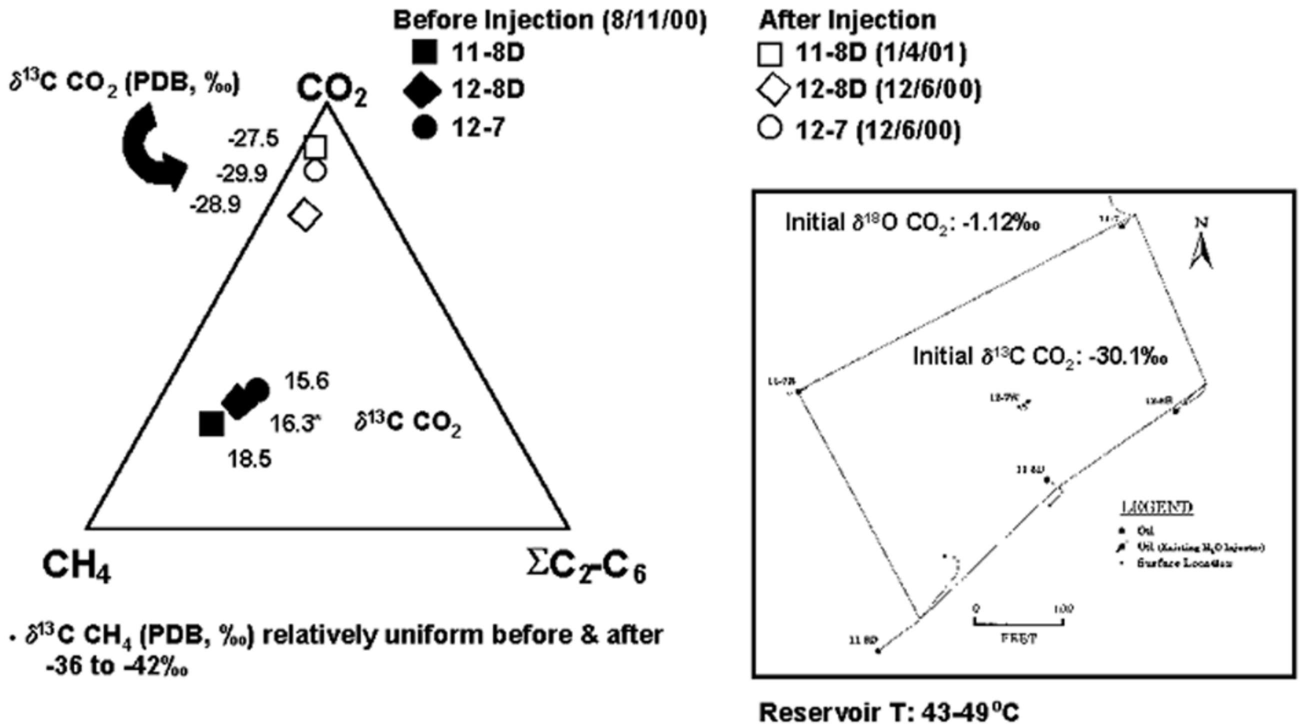

Figure 7. Preliminary isotopic and chemical analyses of gases from the Chevron's Lost Hills, CA injection site.

A final design for the dynamic flow system has been completed (see schematic in Figure 8) which gives us the capability of assessing the relative interactions of gas tracers such as SF_6 and an assortment of perfluorocarbons (PFC's) with a variety of reservoir materials over a range of temperatures (up to ~80^{o}C) and pressures (up to 300 bars) appropriate for proposed injection scenarios. The system, currently under construction, is comprised of several features: (a) carrier gas and He reservoirs, (b) brine reservoir, (c) tracer gas injection volume, (d) gas homogenization reservoirs, (e) brine flow line, (f) sample loop, and (g) gas chromatograph. Helium is used to sparge other gases as well as in the measurement of porosity of the solid contained in the sample loop. The sample coil is 20 feet long and is initially filled with Ottawa sand (20-30 mesh). The sample coil length and diameter can be varied according to the specific application. Brine can be pumped into the coil prior to initiating gas flow. Carrier gas and tracer gas(es) are thoroughly mixed prior to flow. Multiple flow paths (boxes 10 and 11, Figure 8) permit repeated "reloading" of the system with carrier gases that contain different types and amounts of tracer gases.

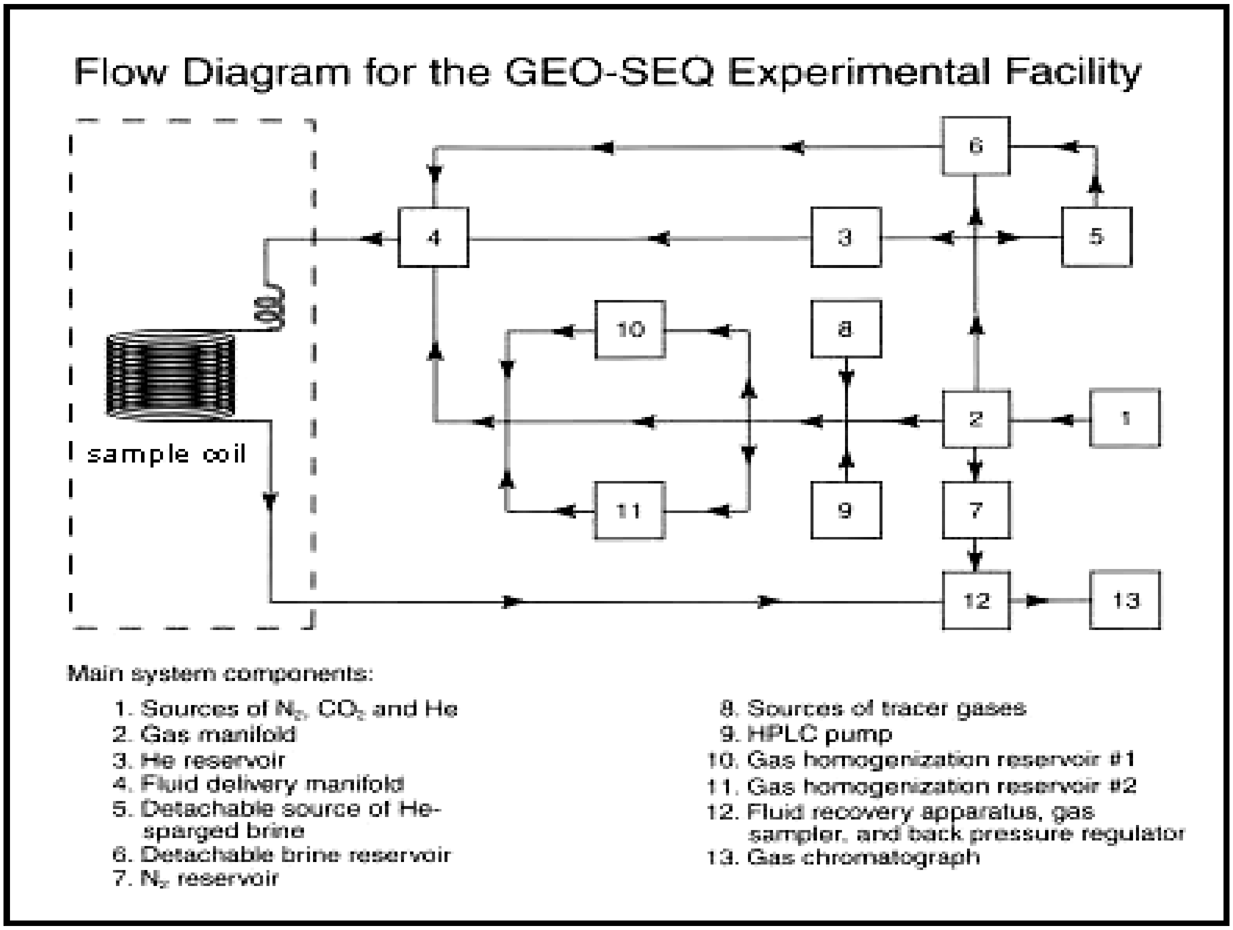

Figure 8. Schematic of dynamic flow system used to test multiple tracers under simulated injection conditions

On the analytical front, three perfluorocarbon tracers (PFT) including perfluoromethyl cyclopentane (PMCP), perfluoromethyl cyclohexane (PMCH), and perfluorotrimethyl cyclohexane (PTCH) are being evaluated together and separately on a gas chromatograph equipped with an electron capture device. Initial tests include sample injections onto two non-polar columns (HP-1 and HP-5) and an $AlOH_2$ column to characterize sensitivity, retention times, and peak resolution. In addition, factors such as column length, internal diameter, and phase thickness have been examined for performance. GC parameters including oven and injector temperature, column flow and head pressure, septum purge flow, and split vent flow were varied to evaluate effects upon separation. In addition, isothermal and temperature programs have been developed and performed according to relative PFT boiling points and current literature. Quality control parameters at this point include triplicate readings of sample injections while observing the standard error among peak areas.

Work Next Quarter : Efforts in the next quarter will focus on four main areas:

1. Continue chemical and isotopic assessment of the next batch of gases sampled at Lost Hills, CA.
2. Initiate CO_2 sorption-desorption experiments using Argonne Premium coals as well as Lost Hills core and mineral end-members, quartz, and calcite, and the Ottawa sand.

3. Initiate a modeling effort using Geochemist's Workbench to assess the magnitude of carbon and oxygen isotope partitioning during gas-brine-mineral reactions relevant to subsurface aquifer formation conditions.
4. Complete construction of flow-through column apparatus and laboratory testing of the applied tracers using the Ottawa sand.

Task C: Enhance and Compare Simulation Models

Subtask C-1: Enhancement of numerical simulators for greenhouse gas sequestration in deep, unmineable coal seams.

Accomplishments:

- Testing of six-coalbed methane reservoir simulators on two test problems have been completed. Discrepancies are being discussed prior to preparation of a report summarizing the work.

Summary:

The goal of this subtask is to improve simulation models for capacity and performance assessment of CO_2 sequestration in deep, unmineable coal seams.

Progress this Quarter : Testing of the first two sets of numerical simulation problems has been completed: (1) problem set 1 is a single well CO_2 injection/production test; and (2) problem set 2 is a five-spot CO_2 injection/production process. The numerical models being tested are CMG's STARS and GEM, GeoQuest's ECLIPSE, BP's GCOMP, CSIRO's SIMEDII and ARI's COMET2. Discrepancies between model predictions (see Figure 9 and 10) are being discussed between participants. Feedback from participants will be gathered to draw the final conclusions. A paper that summarizes the comparison results and describes the current development of the CBM numerical models has been submitted for presentation and publication at the SPE/CERI Gas Technology Symposium (GTS) 2002, Calgary, Alberta, Canada, April 30 – May 2, 2002. A preliminary conclusion is that numerical predictions using a "single porosity approach" and a "dual porosity approach" are quite different (see Figure 9).

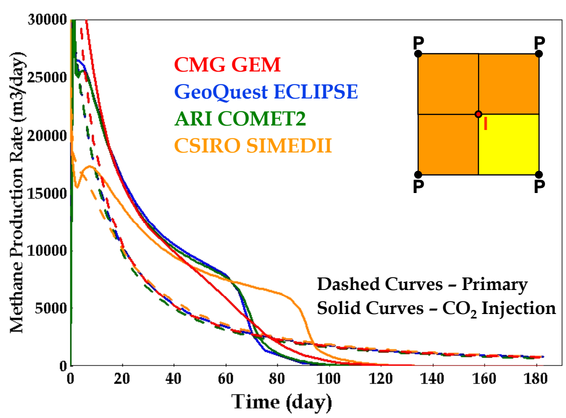

Figure 9. Problem Set 2
Model Comparison (Dual Porosity Approach)

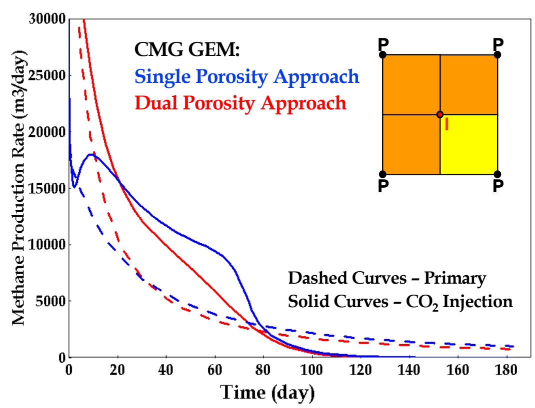

Figure 10. Problem Set 2
Difference between Dual and Single Porosity Approaches

Two sets of numerical simulation problems are currently being tested: Problem set 3 is an enhancement of problem set 2 by taking into account the mixed gas diffusion between the coal matrix and the natural fracture system, and problem set 4 is an enhancement of problem set 2 by taking into account the natural fracture permeability/porosity as functions of natural fracture pressure. Numerical prediction from

CSIRO's SIMEDII (problem set 3) indicates that mixed gas diffusion between the coal matrix and the natural fracture system controlled by the desorption time constants can have a significant effect on the methane gas production rates (see Figure 11).

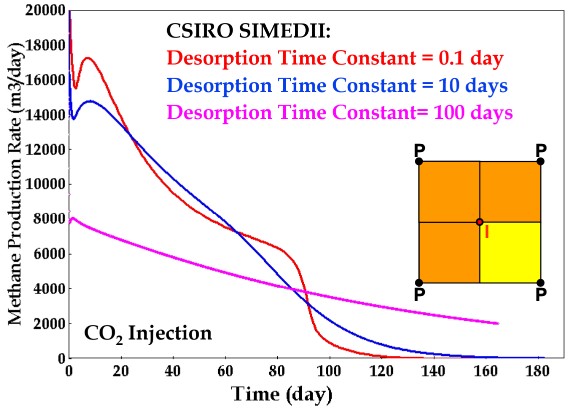

Figure 11. Problem Set 3
Effect of Desorption Time Constant on Methane Production Rate

Field data obtained from a single well micro-pilot test with pure CO_2 injection conducted by the Alberta Research Council (ARC) at the Fenn Big Valley site, Alberta, Canada (see Figure 12) is ready to be released to participants of the model comparison study under the condition that a confidentiality agreement will be signed by the participants before using the data (see Figure 13) for history matching. The micro-pilot test was designed in four stages: (1) CO_2 injection; (2) Shut-in pressure falloff test; (3) Post-CO_2 production; and (4) Shut-in pressure buildup test. The field test was started on June 17, 1998 and was completed after 21 days.

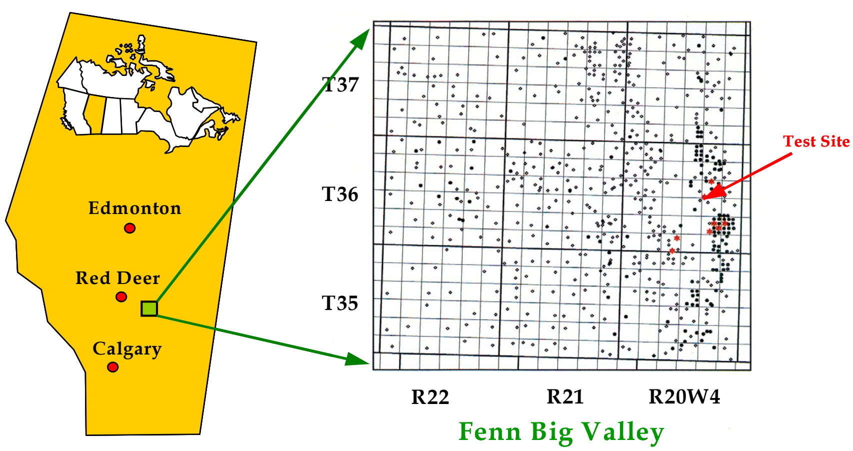

Figure 12. Location of Micro-Pilot Test

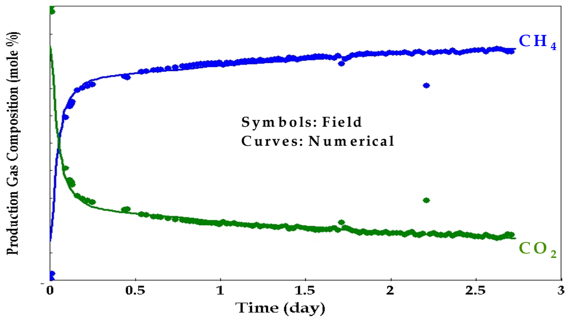

Figure 13(a). Field Data
Well Bottom-hole Pressures

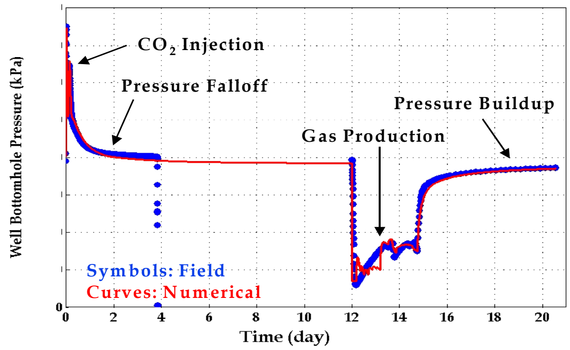

Figure 13(b). Production Gas Composition

Work Next Quarter : Post published results from problem sets 1 and 2 on the ARC website: http://www.arc.ab.ca/extranet/ecbm/ (user name: ecbm and password: coal2).

Post problem sets 3 and 4 on the ARC website: http://www.arc.ab.ca/extranet/ecbm/ after preliminary testing. Complete testing of problem sets 3 and 4.

Continue negotiation with Burlington Resources for the release of field data from their CO_2-ECBM pilot for a problem set which predicts N_2 and CO_2 breakthrough.

Subtask C-2: Intercomparison of reservoir simulation models for oil, gas, and brine formulations

Accomplishments:

- A first workshop on the code intercomparison project was held at LBNL on October 29-30 , 2001.
- The first intercomparison of simulation results by different groups showed reasonable agreement for most problems.
- Detailed reporting requirements for completing the current intercomparison study were developed and agreed upon.

Summary:

The objective of this subtask is to stimulate the development of models for predicting, optimizing, and verifying CO_2 sequestration in oil, gas, and brine formations. The approach involves: (1) developing a set of benchmark problems, (2) soliciting and obtaining solutions for these problems, (3) holding workshops of industrial, academic, and laboratory researchers, and (4) publishing results.

Progress this Quarter : The LBNL group completed simulations for seven of the eight test problems, and presented results at the workshop. Ten groups from six countries are actively participating in the intercomparison study, and nine of these were represented at the workshop (see Table 1). The participant from CSIRO (Australia) was not able to attend for personal reasons but did submit results in electronic form. In addition we had participants from two organizations (Battelle, IIRG - Italy) that are not currently involved in the study, but hope to be able to join in the future. All active groups presented results (see Table 2), and for the most part there was reasonable agreement. An exception was problem 7 (2-D layered brine reservoir), where results seemed to fall into two mutually incompatible classes. Efforts to understand and resolve these discrepancies are ongoing.

The main accomplishment of the workshop was to establish detailed reporting requirements for all of the test problems, and to agree on a schedule that entails submission of results to the LBNL coordinator by February 2002, and a first presentation at the upcoming GHGT-6 meeting in Kyoto, October 2002. There also was a consensus that a final reasonably detailed paper on the intercomparison study should be prepared for submission to an archival journal.

Work Next Quarter : We will complete simulations of the test problems to meet all reporting requirements. We will collect solutions by all participating groups, start documenting them, and submit an abstract for presentation at the Kyoto meeting.

Table 1. CO_2 Code Comparison Workshop

LBNL, Bldg. 90-2063, Monday-Tuesday, October 29-30, 2001

List of Participants

Name	Organization	E-mail
Tony Kovscek	Stanford University, U.S.A.	kovscek@pangea.Stanford.EDU
Kristian Jessen		Krisj@pangea.Stanford.EDU
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David H.-S. Law	Alberta Research Council, Canada	law@arc.ab.ca
Yann Le Gallo	Institut Fran□ais de Petrol, France	Yann.LE-GALLO@ifp.fr
Carl Steefel	Lawrence Livermore National Laboratory, U.S.A.	steefel@llnl.gov
Bryan Travis	Los Alamos National Laboratory, U.S.A.	BJTravis@lanl.gov
Rajesh Pawar		rajesh@lanl.gov
Stephen White	Industrial Research Ltd., Lower Hutt, New Zealand	S.White@irl.cri.nz
Robert Fabriol	BRGM (Geological Survey), France	R.Fabriol@brgm.fr
Neeraj Gupta	Battelle, U.S.A.	gupta@battelle.org
Claudio Calore	CNR - IIRG, Pisa, Italy	calore@iirg.pi.cnr.it
Karsten Pruess	Lawrence Berkeley National Laboratory, U.S.A.	K_Pruess@lbl.gov
Curt Oldenburg		CMOldenburg@lbl.gov
Tianfu Xu		Tianfu_Xu@lbl.gov
Jonny Rutqvist		JRutqvist@lbl.gov
Julio Garc’a		jegarcia@uclink.berkeley.edu
Nicolas Spycher		NSpycher@lbl.gov
Marcelo Lippmann		MJLippmann@lbl.gov
George Moridis		gjmoridis@lbl.gov
Larry Myer		LRMyer@lbl.gov
Chris Doughty		CADoughty@lbl.gov

Table 2. Activity Matrix as of October 30, 2001

Test Problem / Group	1 Stratified Gas	2 Lateral Gas	3 Radial Aquifer	4 Fault Discharge	5 Mineral Trapping	6 Hydro-mechanical	7 Layered Brine	8 CO_2-Oil
LBNL	R, [1]	R, [1]	R, [1]	R, [1]	R, [1]	R, [1]	R, [1]	
LLNL							R, [1]	
LANL			R, [1]	R, [1]	R, [1]	[1]	[1]	[1]
Stanford						?	R, [1]	R, [1]
Alberta	R, [1]	R, [1]	?	?	?			?
Stuttgart						([1])	R, [1]	
IFP	R, [1]	R, [1]	R, [1]	R, [1]	?		R, [1]	[1]
BRGM					R, [1]			
IRL	R, [1]	R, [1]	R, [1]	R, [1]	[1]	?	R, [1]	
CSIRO			R, [1]	R, [1]	?		R, [1]	
Battelle	?	?	?	?			?	

Key: R - results presented at workshop
[1] - plans to do problem by the February 2002 deadline
([1]) - simplified version by February 2002
? - may or may not do the problem

Task D: Improve the Methodology and Information for Capacity Assessment

Accomplishments:

- Different CO_2 sequestration scenarios in the Frio formation were compared based on numerical modeling studies. Predicted gas-phase capacity and its change with time are strongly dependent on the assumed lithology and boundary conditions.

Summary:

The objectives of this task are to: (1) improve the methodology and information available for assessing the capacity of oil, gas, brine, and unmineable coal formations; and (2) provide realistic and quantitative data for construction of computer simulations that will provide more reliable sequestration capacity estimates.

The Texas Gulf Coast was targeted as an area from which a realistic data set could be generated for use in simulation of capacity in brine formations. Location and identifying information were compiled for large industrial CO_2 emitters and geologic data for the Frio and Oakville reservoirs were compiled. A realistic scenario for CO_2 injection into a brine formation was then designed for a site near Baytown, Texas. The capacity of brine formations for storage of CO_2 at the site was assessed using numerical simulation.

Progress this Quarter: Numerical modeling studies continued to examine the capacity of brine formations for CO_2 sequestration. The basic model is a 1 km by 1 km by 100 m thick representation of a shallow portion of the Frio formation, a widespread fluvial-deltaic formation in the Texas Gulf Coast that has been identified as possessing many desirable features for CO_2 sequestration (see previous quarterly reports). The 3-D stochastic model comprises interlayered sands and shales representing barrier cores, distributary channels, washovers, splays and flood plain layers. The upper and lower boundaries of the model are closed to represent continuous sealing shale layers, but shale layers within the model are typically discontinuous allowing buoyancy-driven upward flow of CO_2. Such flow has strong ramifications on the distribution of CO_2 within the model, and consequently also on the capacity.

Figure 14 shows a 3-D cut-away view of the basic model. Note that the upper quarter of the model is nearly pure high-permeability sand (barrier core), whereas the lower three-quarters alternate between sand channels and shales (fluvial-deltaic facies). Having barrier core or wave-dominated delta above fluvial-deltaic is generally common near the top of the Frio, where regional transgression was the order of the day (or million years). Near the top of the Frio, it would be very unlikely for fluvial layers to occur above barrier core/wave-dominated delta intervals.

At the base of the Frio, the reverse is generally true, where barriers and deltas are overlain by prograding delta plains and fluvial systems. The problem for CO_2 sequestration in this setting is that the stratigraphically nearest shale to act as a top seal is several hundred feet upsection, near the top of the Frio. However, it is conceivable that a location could be found, away from fluvial axes, where floodplain shales would be thick and widespread, and might serve as a subregional-scale seal. Such a setting would probably not be the first target for CO_2 sequestration, but it might come into play if one is restricted to a small area (say around a power plant) where the upper Frio is full of oil and gas.

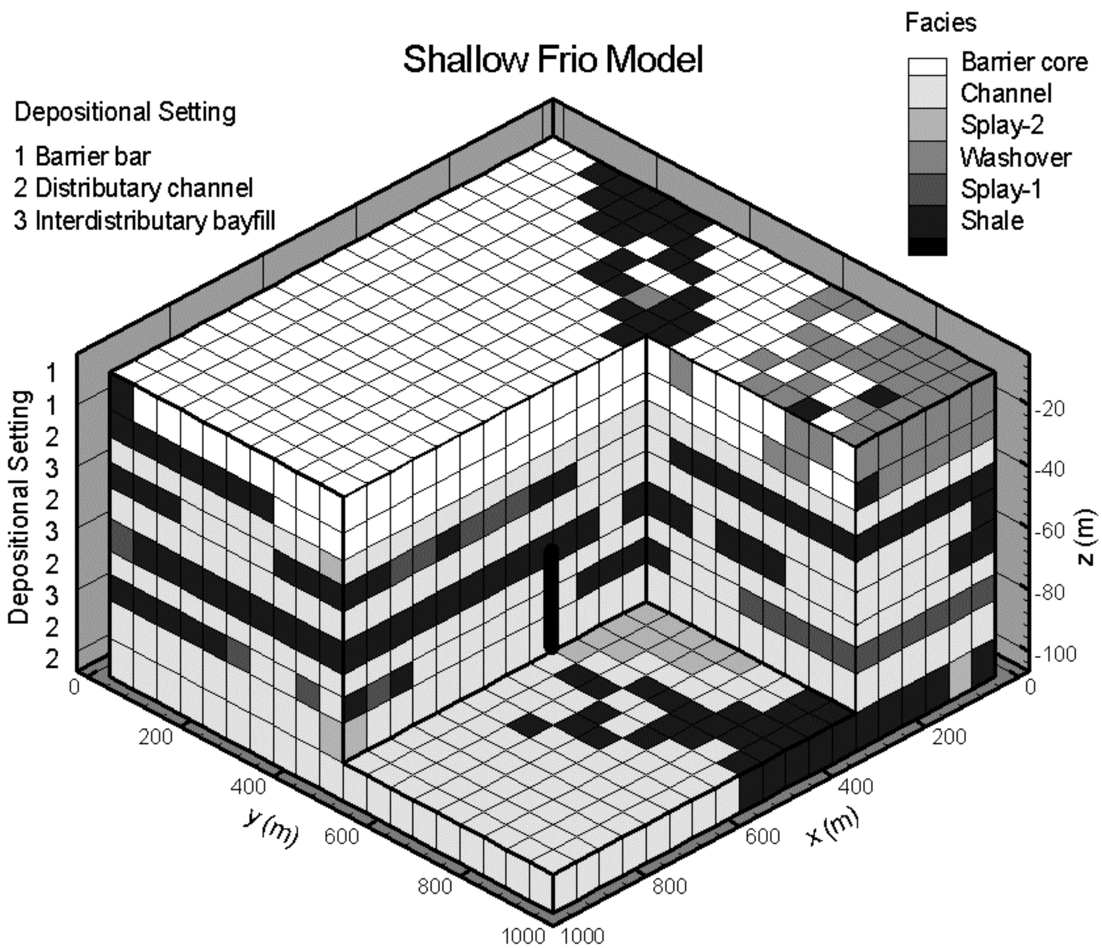

Figure 14. Cut-away view of the shallow Frio model.

Figure 14. shows a new model generally characteristic of the deep Frio. It represents a prograding wave-modified delta. It starts with a delta-front (the barrier bar realizations) at the base that increase in thickness with successively higher layers as accommodation increases, and this is overlain by progressively more proximal facies (distributary channel) then bayfill (shale realizations). This is not a straight progression, in other words, some distributary channel intervals are mixed in between the bar intervals in the lower part, and some shale intervals between distributary channel intervals. This nonlinearity is typical of what is seen in nature.

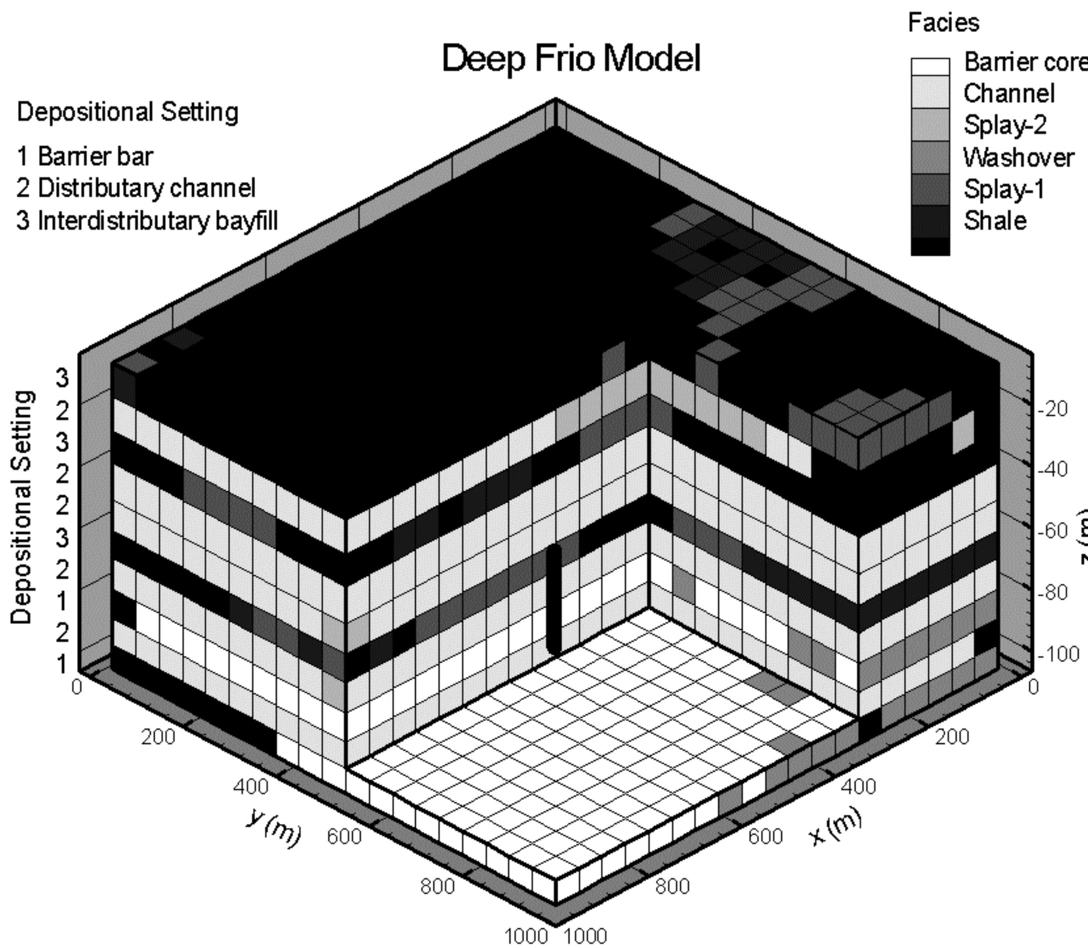

Figure 15. Cut-away view of the deep Frio model.

Figure 15 compares the capacity as a function of time for two shallow Frio sequestration scenarios that inject CO_2 at a constant rate for 20 years and then the system is allowed to evolve with no further injection. In the base case, the injection well is open over the lower half of the model. In the second case, the injection well is open over the entire model thickness. In both cases, CO_2 reaches the lateral boundary of the model after about four years of injection. In the base case, gas-phase capacity continues to increase slowly thereafter, as buoyancy flow moves CO_2 into the high-permeability barrier core sands in the upper portion of the model. In contrast, in the second case, both gas-phase CO_2 and liquid-phase CO_2 (i.e., CO_2 dissolved in the aqueous phase) capacities become nearly constant once the lateral boundary is reached. Thus, a steady state exists in which equal amounts of CO_2 enter and exit the model. After the injection period ends, gas-phase capacity decreases in both cases, but the liquid-phase capacity continues to increase slowly.

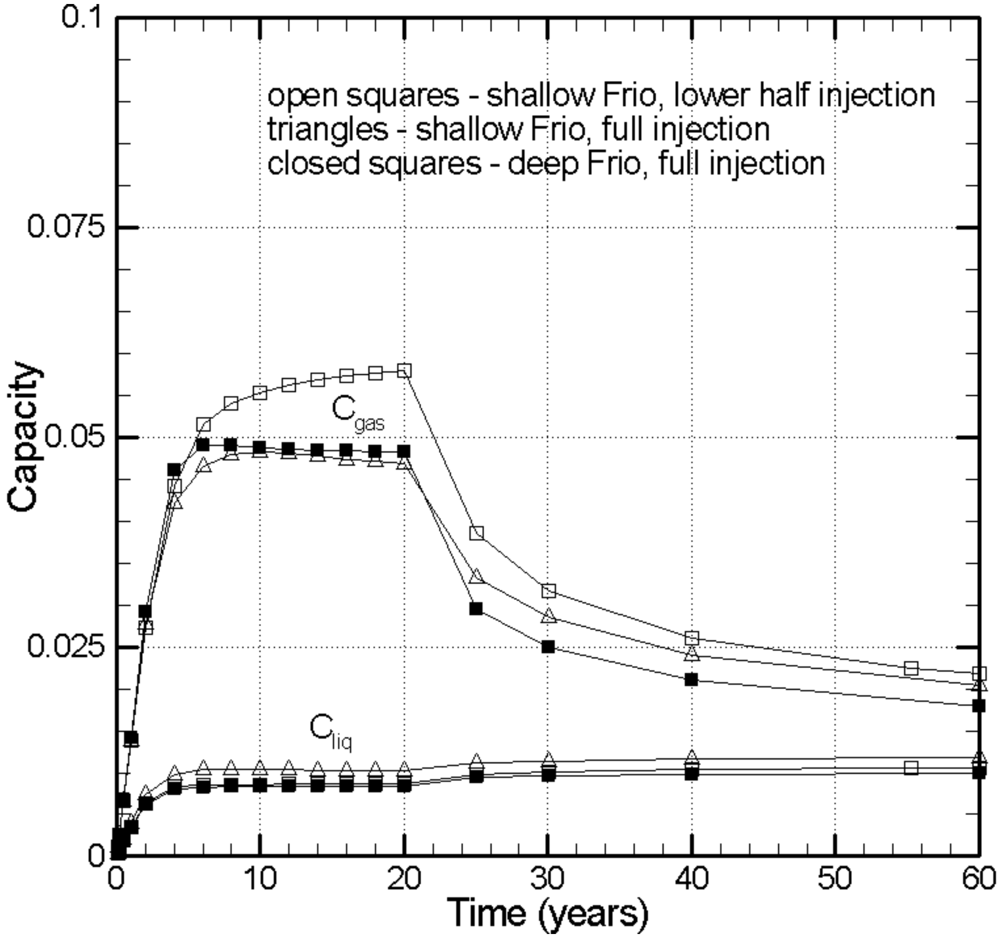

Figure 16. Capacity in the gas phase (C_{gas}) and in the liquid phase (C_{liq}) as a function of time. For each phase, C is the product of intrinsic capacity, geometric capacity factor, heterogeneity capacity factor, and porosity.

An additional simulation study considered a variation on the shallow Frio model in which the shale layers within the model provide continuous seals, essentially eliminating large-scale buoyancy flow. If the same lower-half injection interval is used as for the base case, CO_2 remains entirely confined to the lower half of the model and capacity is much lower than for the base case. However, if a fully penetrating well is used, the CO_2 distribution is similar to that of the base case. Thus, if one could determine how effectively sealed shale layers will be, one could customize the sequestration scenario to optimize capacity.

For the deep Frio model, there is less opportunity for buoyancy flow to effect large-scale movement of CO_2. A sequestration simulation using a fully penetrating well yields similar capacities to those of the corresponding shallow Frio model, as shown in Figure 16.

Two potential limitations of the existing Frio models are currently being investigated. One is the coarse vertical resolution of the simulation grid (one grid layer for each lithologic layer) and the second is the nearness of the lateral constant-pressure boundaries. Several vertically refined grids have been developed, and preliminary indications suggest that for quantitatively accurate capacity predictions, at least two grid layers per lithologic layer are needed. A laterally extensive model is also being developed. It has a variable lateral grid resolution, which will allow both near-well and far-field pressures to be calculated. In addition, the capacity definition (which currently is strongly dependent on the existence of the nearby constant pressure boundaries) can be generalized.

Cost Summary:

	LBNL (Including subcontract to Stanford, TBEG, and ARC)	**LLNL**	**ORNL**
FY02 Funding + Carryover	$262,000	$ 70,700	$ 65,532
Quarterly Cost	$242,000	$ 98,000	$ 86,238
FY02 Cumulative Cost	$183,000	$ 68,000	$ 28,746
Remaining Balance	$ 79,000	$ 27,000	$ 36,786